Sediment Quality Assessment of the Iona Deep-Sea Outfall Area, 2000-2002

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Abstract

The Iona Island Primary Wastewater Treatment Plant is one of five major primary and secondary treatment plants owned and operated by the GVRD. Annual monitoring of the Iona Deep-Sea Outfall and vicinity has been performed since 1986, including two years of pre-discharge monitoring and 15 years of post-discharge monitoring. As determined by effluent dispersion and solids deposition modelling, effluent and effluent solids from the Outfall have a net northward transport due to prevailing currents; therefore, exposure to the Iona discharge is not simply a function of distance relative to the Outfall. Three measures were used to quantify exposure: sediment fecal coliform concentrations, sediment coprostanol concentrations, and estimated maximum annual deposited solids loads. These exposure parameters had strong positive correlations, with similar spatial distributions that peaked north of the outfall, decreasing sharply to the north and south. An analysis of the spatial patterns in sediment concentrations of contaminants of potential concern was conducted. Sediment contaminant concentrations were also compared to relevant marine sediment quality guidelines, reference site and pre-discharge values.

Introduction

The Greater Vancouver Regional District (GVRD) provides wholesale wastewater utility services to its member municipalities. Long-range planning for these services is addressed through a Liquid Waste Management Plan (LWMP). Defined in the LWMP is a role for monitoring as a tool to define environmental needs that in turn determine appropriate levels of service and treatment of wastewaters (GVRD 2001).

The Iona Island Primary Wastewater Treatment Plant (WWTP) is one of five major wastewater treatment works owned and operated by the GVRD. The Iona Plant provides primary treatment for a serviced area of approximately 14,000 hectares and a population of about 560,000. In 1988, the Iona Deep-Sea Outfall was put into service and replaced the previous surface discharge at Sturgeon Bank. The new outfall discharges primary treated municipal effluent from the Iona Island Wastewater Treatment Plant at an average depth of about 90 m into the Strait of Georgia, some seven kilometers west of the Iona Island shoreline. The discharged plume is trapped below the surface water due to density stratification, likely throughout the year with modelled plume trapping depths from about 25 to 90 m (Hodgins and Hodgins 1999). The treatment plant effluent is not disinfected.

Annual monitoring of the Iona Outfall and vicinity has been performed since 1986 and has included a variety of components (e.g., chemical and physical analyses of effluent, receiving water, sediment and biota; bacteriological analysis of water and sediment; histopathology; sediment toxicity testing; infaunal community structure analysis). The overall monitoring program is repeated approximately every five years.

An independent review of the monitoring results was conducted in 1998 (Wilson et al 1999), including an evaluation of the proposed third-cycle monitoring plan and recommendations for conducting a hypothesis-based monitoring program and long-term trend analysis. These recommendations were reflected in the design of the third cycle of monitoring (McPherson et al 2001). Beginning in 2000, the sampling locations were modified to a 16-station transect extending approximately 7 km north and 9 km south of the outfall, on a general-north south direction along the 80-m depth contour. The sampling grid was optimized to carry out sediment benthos surveys.

Physico-chemical and microbiological characterization of surficial sediment collected within the Iona study area were used: to determine the spatial extent and distribution of concentrations of contaminants; compare contaminant concentrations with relevant sediment quality guidelines (SQGs), as well as to background and historical values; and

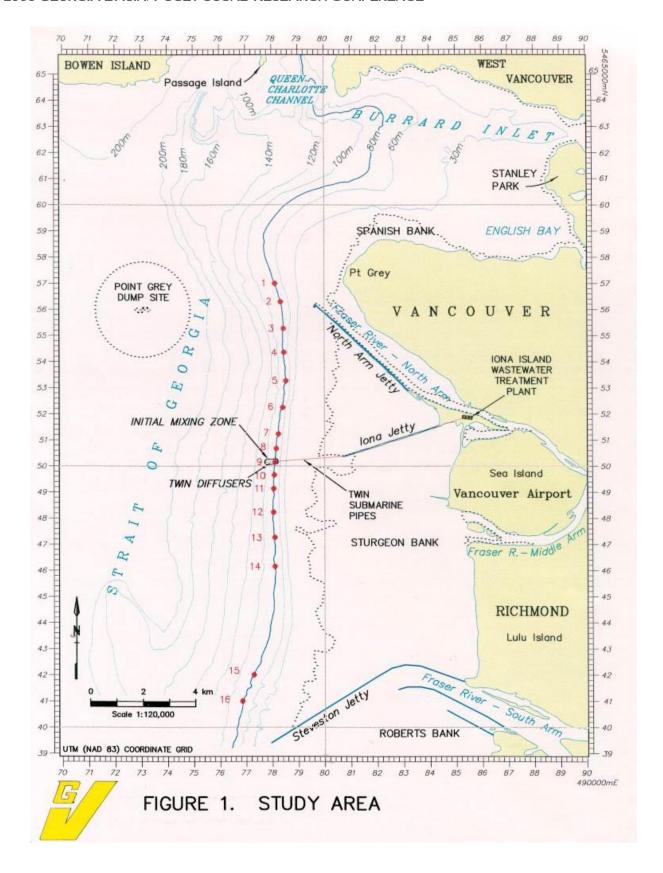


Figure 1. Study area including locations of sampling stations.

evaluate influences of confounding factors in a multiple contaminant environment. Concentrations of contaminants and conventional parameters were also incorporated into subsequent analyses of the benthic community to evaluate potential effects in the receiving environment; these results are described in a report by Bailey et al. (2003).

Methods

Sampling

The field sampling program was carried out by Integrated Resource Consultants Inc. (Richmond, BC) and Seaconsult Marine Research Ltd. (Vancouver, BC). Sediment sampling coincided with the Fraser River winter low flow period, prior to freshet (i.e., late March). Sampling locations were spread in a north-south orientation, with one site located at the nearshore side of the diffusers (Station 9), eight sites located north of the diffusers (Stations 1 to 8), and seven sites located south of the diffusers (Stations 10 to 16). Locations of the sampling stations are shown in Figure 1. A TrimbleTM Pathfinder Pro XLR differential global positioning system provided real time positions at <1-m accuracy.

Sample collection methods were based on Puget Sound Protocols (PSEP 1987, 1997). The sediment sampler was a 0.1-m² area Van Veen grab, modified with hinged top screens with rubber flaps to minimize sediment disturbance during retrieval and allow access to the upper surface of the substrate without removing the sample from the sampler.

Three grabs collected from each of the sampling stations were used for sediment chemistry and bacteriology. The contents of the grab were visually examined and observations of the colour, odour, texture and other characteristics were recorded. Onboard the vessel, the upper screen of the sampler was opened to determine that a representative sample had been obtained (80 to 100% filled with sediment). Prior to subsampling for bacteriology and chemistry samples, a sterile polyethylene tube was used to remove the overlying water by syphoning. Separate subsamples of sediment were removed from the top 2-cm of each grab for analysis of bacteriology and selected chemical parameters, including moisture, total organic carbon (TOC), total organic nitrogen (TON), total volatile solids (TVS), acid volatile sulphide (AVS), and simultaneously extractable metals (SEM).

After the bacteriology and sediment chemistry sub-samples were removed, the remaining top 2-cm layer of sediment from the three grabs from each station was composited in a pre-cleaned stainless steel bowl. Aliquots of sediment from each composite were analyzed for conventional parameters (moisture, TOC, TVS, particle size), metals and trace organics.

Sample containers were transported in coolers containing freezer packs and plastic wrap to keep the samples chilled, but not frozen. Samples were delivered to the analytical laboratories within 16 h of sediment collection. The sampler was scrubbed with a phosphate-free laboratory detergent and rinsed with seawater between sites.

Analyses

Fecal coliform measurements were conducted by the GVRD Quality Control Laboratory, Microbiology Section (Burnaby, BC); conventionals and metals analyses were performed by ALS Environmental (Vancouver, BC), with the exception that the total volatile solids (TVS) and particle size analyses were conducted by Pacific Soils Analysis Ltd. (Richmond, BC); and trace organic analyses were performed by Axys Analytical Services Ltd. (Sidney, BC).

Sediment bacteriology

Sample preparation was done using Methods 9221B and 9221E, and analysis to evaluate fecal coliforms was conducted using Method 9221C of Standard Methods (APHA 1998).

Conventionals

Sediment moisture analysis was carried out gravimetrically following drying at 103°C for a minimum of six hours. Total Volatile Solids (TVS) were measured using methods based on McKeague (1978). Total carbon, TOC and inorganic carbon were analysed in accordance with USEPA Method 9060A (USEPA 1986a). TON was measured using methods based on McKeague (1978), and was determined as the difference between total nitrogen and ammonia nitrogen.

Particle size

Particle size distribution was carried out using a method described in Walton (1978), to determine the proportions of material present in each of the following particle size categories: gravel (>2.00 mm), very coarse sand (<1.00 - 0.500 mm), medium sand (<0.500 - 0.250 mm), fine sand (<0.250 - 0.125 mm), very fine

sand (<0.125 - 0.0625 mm), coarse silt (<0.0625 - 0.0312 mm), medium silt (<0.0312 - 0.0156 mm), fine silt (<0.0156 - 0.0078 mm), very fine silt (<0.0078 - 0.0039 mm), clay (<0.0039 mm).

Metals and AVS/SEM

Analyses of sediment metals concentrations were conducted following preparation and digestion procedures adapted from USEPA Methods 3050B (USEPA 1986a). Arsenic was measured using hydride vapour atomic absorption spectrometry (HVAAS); cadmium, lead and silver were analysed using flame atomic absorption spectrometry (FAAS); mercury was measured with cold vapour atomic absorption spectrometry (CVAAS); and chromium, copper, nickel and zinc were measured using inductively coupled plasma-optical emission spectrophotometry (ICP-OES).

Acid volatile sulphide (AVS) and simultaneously extractable metals (SEM) were evaluated in accordance with methods described by USEPA (1991a). Detected concentrations of individual SEMs were summed to provide an overall "sum of SEM" concentration for each of the 16 stations and the ratio of SEM:AVS was also calculated for each station. Concentrations of nine acid-extractable metals (arsenic, cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc) were determined by atomic absorption spectrophotometry (AAS; Method 7000 series, USEPA 1986a) and ICP-OES (Method 6010B, USEPA 1986a).

Trace organics

Samples used for trace organic analyses were homogenized and subsampled for analysis within 24 hours of receipt and then stored at -20°C prior to conducting analyses. For each parameter, concentrations were corrected for the recovery of surrogate standards and calculated on a dry weight basis using isotope dilution quantification. Concentrations of parameters that were below detection were reported in terms of sample-specific detection limits (SDLs), which correspond to the "area reject" (determined from the ion chromatograph as the area of a peak with height three times the maximum height of the noise). For a given parameter, these SDLs may differ by as much as a factor of 10-fold from one sample to another.

Measurement of PCBs as Aroclors and as congeners were conducted using methods based on USEPA Method 1668A, which uses high resolution mass spectrometry to evaluate all 209 PCB congeners. Each Aroclor was determined as the sum of three to five predominant congeners by quantifying the individual congeners, summing them and multiplying by a predetermined factor.

Chlorobenzenes and chlorinated pesticides were analyzed using procedures based on USEPA (1982, 1986b and 1999), Mullin et al. (1984), Smith (1981), and Stalling et al. (1979). The majority of the targets were analysed using high resolution gas chromatography with low resolution mass spectrometric detection (HRGC/LRMS); however, the most polar pesticides were analysed using high resolution gas chromatography with electron capture detection (HRGC/ECD).

Analyses for nonylphenol and its ethoxylates were conducted using procedures based on Lee and Peart (1995). The extract was analyzed by HRGC/LRMS.

Methodology for the analyses of PAHs and alkylated PAHs were based on Cretney et al. (1980), Cretney (pers. comm.), and USEPA (1986b). Procedures for analyses of sterol biomarkers were based on Eganhouse et al. (1988) and Chalaux et al. (1995). The raw extract was fractionated on silica gel into medium polar (F2) and most polar (F3) fractions. The F2 fraction was analyzed for PAHs and alkylated PAHs by HRGC/LRMS and the F3 faction was derivatized and analyzed by HRGC/LRMS for selected sterol (estradiol) compounds. PAHs targeted for determination included: 17 parent PAHs consisting of 6 low-molecular weight PAHs (LPAHs) and 11 high-molecular weight PAHs (HPAHs), selected alkylated PAHs, and dibenzothiophenes.

Phthalate esters were measured using the same general methodology used for PAH and sterol analyses; however, these analyses were conducted separately because the phthalate esters eluted into the F3 fraction, creating quantification obstacles that were only overcome by conducting a separate analysis.

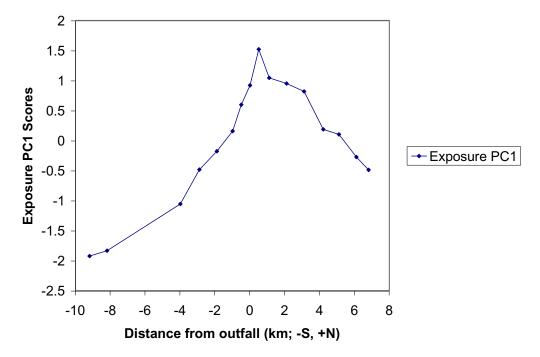


Figure 2: Spatial distribution of the first Exposure Principal Component scores (Exposure PC1).

QA/QC

A detailed Quality Assurance/Quality Control program was followed throughout the sampling and analysis. This included following specific procedures (PSEP 1987, 1997): written observations of the time of collection, weather conditions (precipitation, wind speed and direction), tidal height, vessel drift and direction, vessel position during sediment sampling, depth, descriptions of sample contents, sampling efficiency, and sample appearance; and testing of field QA/QC samples (transportation blanks and duplicate aliquots) concurrently with the regular samples for chemical and bacteriological analyses.

Statistical Analyses

Exposure to the Iona discharge is not a simple function of distance from the outfall because the effluent and effluent solids are transported predominantly to the north with prevailing currents. Three measures of exposure were used: estimated maximum annual deposited solids loads (from Hodgins and Hodgins, 2000); geometric mean sediment fecal coliform concentrations; and sediment coprostanol concentrations (coprostanol is a hormone associated with bacteria in the mammalian gut).

The solids loads provide a general estimate of exposure to the discharge, assuming that sediment contamination occurs largely via deposition of effluent particles. Fecal coliforms and coprostanol should be relatively specific to the discharge, especially in an offshore area where there are few other potential sources of these markers (e.g., agricultural run-off).

Principal Components Analysis (PCA) was used to derive a composite exposure measure from the three exposure indicators. The variables were \log_{10} transformed prior to analyses. Station scores along the major axis (Principal Component 1 [PC1]) of covariance among the three exposure variables were used as a measure of exposure for further analyses (Figure 2). The scores are weighted sums or means of the original variable values; the \log_{10} transformation eliminated differences in measurement scales.

PCA was also used to derive composite measures of contaminant concentration for further analyses. As noted above, PC1 identifies the major axis of covariance among the original variables (e.g., metals concentrations). The minor axis, or PC2, identifies the next largest axis of covariance orthogonal to (independent of) PC1. Compounds that were undetected at more than three (out of 16) stations were excluded from this analysis. Remaining concentrations reported as "undetected" were converted to one-half of their sample-specific DL for parametric analyses (e.g., PCA) and to 0 (i.e., tied for the lowest rank) for non-parametric analyses. This approach minimized the effect of <DL values on the overall statistical analysis and any related conclusions.

PCBs were analyzed separately from other organics because 132 PCB congeners, groups of congeners, or Aroclor mixtures were detected at most stations, compared with 49 other organics. Consequently, a PCA based on all organics, including PCBs, would have been driven largely by relationships among the dominant group (PCBs), which would have obscured relationships of interest among the other organic compounds.

Basic steps in analysis of the individual conventional parameters, and the summary measures (i.e., PC scores) for metals and organics were:

- 1. Spearman rank correlations (r_s) calculated between the sediment quality variables (e.g., metals PC1 and PC2) and Exposure PC1. This step identified the parameters most (or least) closely associated with the discharge.
- 2. Spearman rank correlations (r_s) calculated between the sediment quality variables and northings (i.e., position along the N-S axis). This test for the presence of a north-south gradient identified parameters that may have been affected by factors other than the Iona discharge (i.e., confounding effects).
- 3. The above analyses were repeated for individual parameters to determine if the parameters included in the PC scores exhibited similar spatial distributions, and to examine specific parameters of interest.

Selected parameters which were detected at every station in 2000, 2001 and 2002 were also analysed to evaluate the consistency of spatial differences among stations and the overall patterns of contamination from the Iona discharge during this period.

Results

Data from the sediment monitoring program are described below with tables and figures to illustrate key points. The detailed compilations of raw data can be found in Bailey et al. (2003).

Sediment bacteriology

Geometric-mean fecal coliform counts for surficial sediment samples ranged from 3.6 to 3,300 MPN/g wet weight, as summarized in Table 1. The highest fecal coliform counts were associated with samples collected from 0.5 km north of the outfall diffusers (Station 8) and on the nearshore side of the diffusers (Station 9). The lowest counts were measured in samples taken at Stations 15 and 16, respectively located 8.2 and 9.2 km south of the outfall.

Conventionals

Data for conventional parameters are summarized in Table 1. Mean moisture content ranged from 28.6% to 49.0%. Moisture content was lowest at stations near the outfall diffuser and at the two northernmost stations. Average concentrations of TOC ranged from 0.69% to 1.27%, TVS concentrations ranged from 2.6% to 4.5% and mean TON concentrations ranged from 0.05 to 0.12 mg/kg. The sediments were comprised primarily of fine-grained materials (i.e., silt and clay), except for the two northernmost stations (Stations 1 and 2) which contained higher proportions of sand (64.2 and 46.8%, respectively). Sediments from Station 9 (the outfall) also contained a slightly higher proportion of sand (34.2%). The percentage of fines (silt and clay) ranged from 35.8% to 93.6%.

Table 1. Summary of concentrations of conventional parameters measured in surficial sediment samples collected in 2002. Data are presented as ranges for the stations indicated.

	Stns. 1-4	Stns. 5-8	Stn. 9	Stns. 10-12	Stns. 13-16
	far- to mid-field (4 to 7 km N of Outfall)	near-field (0.5 to 3 km N of Outfall)	Outfall	mid-field (0.5 to 2 km S of Outfall)	far-field (3 to 9 km S of Outfall)
Fecal coliforms (MPN/g wet wt.)	33 – 180	580 - 3300	1300	70 - 300	4 - 40
Moisture (% wet wt.)	32 - 46	45 - 48	41	43 - 45	41 - 50
TOC (% dry wt.)	0.6 - 1.2	1.1 - 1.2	0.9	0.7 - 1.0	0.7 - 1.1
TVS (% dry wt.)	2.3 - 5.2	5.3 - 5.6	4.5	4.6 - 4.9	4.3 - 6.4
TON	0.05 - 0.10	0.12	0.08	0.09	0.08 - 0.10
(% dry wt.) Fines: silt+clay (% dry wt.)	36 - 90	83 - 93	66	77 - 85	72 - 94

Metals and AVS/SEM

Arsenic, cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc were detected in every sample (Table 2). Antimony, bismuth, molybdenum, selenium, thallium and tin were not detected in any samples, and beryllium was only detected (at its DL) in one sample.

Concentrations of SEM cadmium, lead and mercury were below their respective detection limits in samples from all 16 sites. Stations 1, 2, 12 and 16 exhibited SEM:AVS ratios >1. Mean AVS concentration in the sediment chemistry grab samples ranged from 0.2 μ mol/g on a dry weight basis at Station 1 (6.8 km N of the outfall) to 11.7 μ mol/g at Station 8 (0.5 km N of the outfall). Mean AVS concentrations were <2.0 μ mol/g at stations located between 1.0 and 9.2 km south of the outfall, increased at Station 10 (0.5 km S of the outfall), peaked at Station 8, and then declined to <2.0 μ mol/g at Stations 1 to 3 (5.1 to 6.8 km N of the outfall). These data are also summarized in Table 2.

Table 2. Summary of concentrations (mg/kg dry wt., except AVS & SEM: μmol/g dry wt.) of a subset of metals measured in surficial sediment samples collected in 2002. Data are presented as ranges for the stations indicated.

	Stns. 1-4	Stns. 5-8	Stn. 9	Stns. 10-12	Stns. 13-16
	far- to	near-field	Outfall	mid-field	far-field
	mid-field	(0.5 to 3		(0.5 to 2 km	(3 to 9 km S
	(4 to 7 km N	km N of		S of Outfall)	of Outfall)
	of Outfall)	Outfall)			
Arsenic	5.4 - 7.1	7.4 - 7.7	6.5	6.4 - 6.9	6.5 - 7.6
Cadmium	0.05 - 0.20	0.28 - 0.36	0.21	0.10 - 0.18	0.11 - 0.14
Chromium	39 - 53	51 - 57	50	50 - 52	51 - 57
Copper	24 - 45	45 - 50	34	35 - 36	33 - 40
Lead	6 - 11	11 - 12	9	9 - 10	8 - 11
Mercury	0.05 - 0.09	0.09 - 0.12	0.08	0.06 - 0.07	0.05 - 0.07
Nickel	31 - 42	45 - 48	43	43 - 45	47 - 51
Silver	0.19 - 0.45	0.51 - 0.58	0.34	0.22 - 0.28	0.12 - 0.21
Zinc	51 - 80	82 - 88	69	71 - 74	69 - 82
AVS	0.2 - 2.6	5.6 - 11.7	3.2	0.6 - 5.4	0.4 - 1.5
Sum of SEM	0.43 - 0.75	0.82 - 0.89	0.72	0.58 - 0.72	0.44 - 0.70
SEM:AVS ratio	0.29 - 2.24	0.07 - 0.16	0.22	0.13 - 1.19	0.35 - 1.58

Sediment organics

Concentrations of trace organics measured in the sediment samples are summarized in Table 3 and expressed in units of $\mu g/kg$, on a dry weight basis. Total concentrations for a given group of substances were calculated as the sum of constituent concentrations of detected compounds that met quantification criteria.

Of the 10 chlorobenzene compounds analysed, one compound (1,3,5-trichlorobenzene) was not detected in any of the station samples, and five other compounds or groups of compounds (1,3-dichlorobenzene, 1,2,3-trichlorobenzene, 1,2,3,5/1,2,4,5-tetrachlorobenzene, 1,2,3,4-tetrachlorobenzene, and pentachlorobenzene) were detected in one to four samples. 1,4-dichlorobenzene and 1,2,4-trichlorobenzene were detected at all 16 stations and ranged from 0.808 to 6.5 μ g/kg and 0.234 to 1.78 μ g/kg, respectively. 1,2-dichlorobenzene was detected at seven stations and hexachlorobenzene was detected at 14 stations. Total chlorobenzenes ranged from 1.88 μ g/kg at Station 15 (8.2 km S of the outfall) to 8.08 μ g/kg at Station 4 (4.2 km N of the outfall).

In general, organochlorine pesticides were not frequently detected; only beta-HCH, delta-HCH, oxychlordane, p,p'-DDE and trans-nonachlor were detected in samples from one or more stations. Beta-HCH was only detected at Station 6, delta-HCH was detected at Stations 1 through 7, oxychlordane was detected at two stations (Stations 2 and 10), p,p'-DDE was detected at 8 of 16 stations, and trans-nonachlor was only detected at Station 9 (at the outfall diffusers). Concentrations of total chlorinated pesticides ranged from 0.144 to 1.633 µg/kg; no chlorinated pesticides were detected at Stations 12 or 15.

The three commercial mixtures of PCBs evaluated (referred to as Aroclor 1242, 1254 and 1260) were detected at all 16 stations; concentrations of Aroclor 1242 ranged from 0.250 to 0.590 µg/kg, Aroclor 1254 ranged from 0.340 to 0.980 µg/kg and Aroclor 1260 ranged from 0.190 to 0.840 µg/kg. A suite of 209 PCB congeners, which included nonorthosubstituted or coplanar PCBs (e.g., PCB #77, #126, and #169), were also evaluated individually. Of the 209 PCB congeners evaluated (several congeners co-eluted as more than one PCB), 146 were detected in one or more sample, 10 congeners were detected in \leq 25% of the samples, and 113 were detected in \geq 75% of the samples. The largest number of PCB congeners (131) was detected at Station 9 (at the outfall diffusers) and the lowest number (97) was measured at Station 16. Concentrations of total PCBs ranged from 0.710 µg/kg at Station 1 to 2.00 µg/kg at Station 7.

Coplanar PCB #77 was detected at all 16 stations at concentrations ranging from 0.0028 to 0.0086 $\mu g/kg$. Coplanar PCB #126 was detected at 10 stations at concentrations ranging from 0.00012 to 0.0032 $\mu g/kg$. Coplanar PCB #169 was only detected at Station 9 (0.0013 $\mu g/kg$) and Station 4 (0.00022 $\mu g/kg$).

Nonylphenol was detected in sediments from all 16 stations; concentrations ranged from 12 to 205 μ g/kg. Nonylphenol monoethoxylate (NP1EO) and nonylphenol diethoxylate (NP2EO) were detected at Stations 1 through 8, and Stations 1 through 12, respectively.

Five of the LPAH compounds (naphthalene, acenaphthene, fluorene, phenanthrene and anthracene) were detected in all of the samples, while acenaphthylene was detected in 11 samples. The dominant LPAHs found in the sediments were phenanthrene (range: $20 - 57 \mu g/kg$), naphthalene (range: $6.3 - 18 \mu g/kg$), and anthracene (range: $3.9 - 16 \mu g/kg$). Concentrations of total LPAHs ranged from 43 to 91 $\mu g/kg$.

Each one of the targeted HPAH compounds was detected in most or all of the samples, except that dibenzo[ah]anthracene was only detected at Station 16 (it was also detected, but failed to meet quantification criteria in 12 other samples). Benzo[a]anthracene was detected at 10 stations, benzo[e]pyrene at 13 stations, and indeno[1,2,3-cd]pyrene at 12 stations. The remaining 7 of the 11 measured HPAH compounds were detected at all 16 stations. Concentrations of total HPAHs ranged from 167 µg/kg at Station 1 (6.8 km N of the outfall) to 758 µg/kg at Station 9 (outfall diffusers).

Total PAH concentrations in samples ranged from 214 μ g/kg at Station 12 (1.9 km S of the outfall) to 849 μ g/kg at Station 9 (outfall diffusers). The largest contribution to total PAHs was due to HPAH compounds.

Measured alkyl-PAH compounds (C1:C4 alkylated naphthalenes and C1:C4 alkylated phenanthrenes/anthracenes) were detected in all 16 samples; total alkylated PAH concentrations ranged from 195 to 452 µg/kg.

Dibenzothiophene and (C1:C2) alkylated dibenzothiophenes were detected in most or all of the samples. Concentrations of dibenzothiophene ranged from 1.6 μ g/kg to 3.6 μ g/kg. The ratio of the sum of concentrations of (C1:C2) alkylated dibenzothiophenes to the parent dibenzothiophene was greater than one for all stations. Maximum concentrations of alkylated dibenzothiophenes occurred at Station 8 (0.5 km N of the outfall).

All six targeted phthalate ester compounds were observed in the samples; however, only four compounds exhibited concentrations that met quantification criteria in one or more samples. Diethyl phthalate was detected at all stations, di-N-butyl phthalate was detected in 10 samples, butyl benzyl phthalate was detected in 8 samples, and bis-(2-ethylhexyl) phthalate was detected in all 16 samples. Phthalate ester data (Table 3) should be used with caution because phthalates are ubiquitous compounds in the environment and a common contamination problem encountered during field sampling and laboratory analysis.

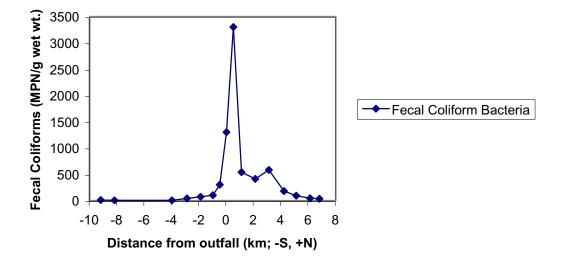
Table 3. Summary of concentrations (μ g/kg dry wt.) of trace organics measured in surficial sediment samples collected in 2002. Data are presented for a subset of organics parameters as ranges for the stations indicated.

	Stns. 1-4	Stns. 5-8	Stn. 9	Stns. 10-12	Stns. 13-16
	far- to mid- field (4 to 7 km N of Outfall)	near-field (0.5 to 3 km N of Outfall)	Outfall	mid-field (0.5 to 2 km S of Outfall)	far-field (3 to 9 km S of Outfall)
Total Chlorobenzenes	2.5-8.1	4.7 - 6.8	3.5	2.9 - 4.4	1.9 - 3.6
Total Organochlorine Pesticides	0.32-1.59	0.43 - 1.63	0.29	ND - 0.29	ND - 0.18
Total PCB Congeners	0.7 – 1.9	1.4 - 2.0	1.4	0.7 - 1.4	0.9 – 1.1
Arochlor 1242	0.2 - 0.6	0.4 - 0.50	0.4	0.2 - 0.5	0.3 - 0.4
Arochlor 1254	0.3 - 1.0	0.7 - 1.0	0.7	0.4 - 0.7	0.4 - 0.5
Arochlor 1260	0.2 - 0.6	0.5 - 0.8	0.4	0.2 - 0.3	0.2 - 0.3
Diethyl Phthalate	2.1-4.2	4.1– 10	3.9	4.0 - 6.6	4.5 - 7.0
Bis-(2ethylhexyl) Phthalate	260 – 580	630 – 840	400	240 – 290	230 – 300
Total LPAHs	58 – 66	49 – 81	91	46–48	43 – 52
Total HPAHs	276 – 309	167 – 339	758	168 – 196	178 – 227
Total Alkylated PAHs	340 – 452	195 – 358	344	270 – 281	272 – 345
Total Alkylated Dibenzothiophenes	13 – 21	9 – 19	18	8 – 10	8 – 11
Coprostanol	1400 – 3200	5700-10000	3500	1400 – 3200	460 – 1100
Epicoprostanol	100 – 270	430 – 550	230	120 – 210	66 – 100
4-Nonylphenol	17 – 62	71 – 205	73	36 – 61	12 – 34
NP1EO	18 – 78	49 – 103	32	6 – 14	<2 – <4
NP2EO	18 – 74	46 – 154	<7	<4 – <6	<8 – <12

Only 9 of 22 targeted estradiol and sterol compounds were detected in one or more of the samples. Coprostanol concentrations ranged from 460 to $10,000 \mu g/kg$ at Station 8; concentrations were generally highest between Stations 5 and 10. Epicoprostanol concentrations ranged from 66 to 550 $\mu g/kg$.

Relationships of the parameters to the discharge

Sediment coliform and coprostanol concentrations were significantly positively correlated with estimated solids loads, and with each other. Exposure PC1 explained 90.8% of the variance in these three variables over the sampling stations, suggesting that it was a reasonable measure of exposure. The spatial distributions of these two parameters are shown in Figure 3 (bottom panel) for data collected in 2000, 2001 and 2002. In general, the highest values were obtained at stations proximate to the discharge, a decreasing trend was observed with distance from the outfall, and elevated levels were observed in northerly stations relative to southerly stations at equivalent distances from the discharge.



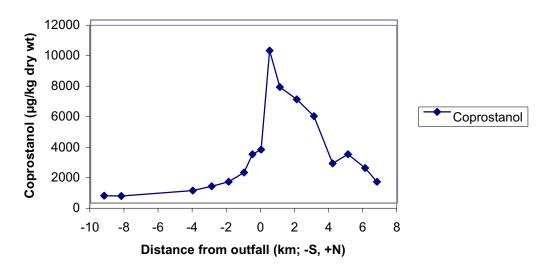


Figure 3. Spatial distribution of sediment fecal coliform (top panel) and sediment coprostanol (bottom panel)

Fines content, moisture content, TOC and TVS were not significantly correlated with either Exposure PC1 or northings, indicating the spatial patterns of these conventionals differed from the exposure pattern, and there were no apparent north-south (N-S) gradients for these parameters. Both AVS and TON were positively correlated with Exposure PC1, but not with northings. Spatial distribution of AVS is shown in Figure 4.

Concentrations of the 22 metals analyzed (the 9 individual metals, plus 13 detected metals from the multi-element scan) were all positively correlated with the first principal component (Metals PC1) derived from those elements. Metals PC1 accounted for 77% of the total variation in metal concentrations, and can be considered a general measure of "total metal" concentrations. The second principal component (Metal PC2) accounted for 60% of the remaining variation (14% of overall variation). Metals PC2 was significantly positively correlated with mercury, cadmium and silver concentrations. These data indicate that metals generally followed a common spatial distribution, and that deviations from the common pattern could be attributed primarily to mercury, cadmium and silver.

Spatial distributions of Metals PC1 and Metals PC2 are shown in Figure 5. Metals PC1 scores were not significantly correlated with either Exposure PC1 or northings; however, metals PC2 scores were significantly positively correlated with Exposure PC1. Mercury, cadmium and silver were the metals most strongly correlated with Exposure PC1 (all three metals exhibited $|r_s| \ge 0.78$).

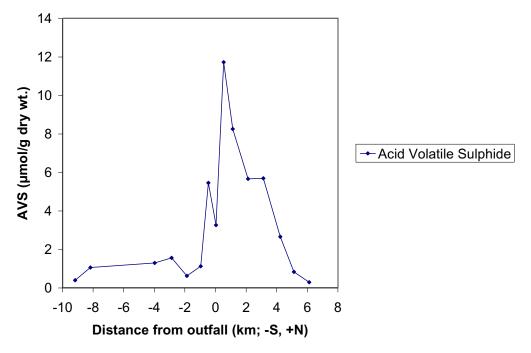


Figure 4. Spatial distribution of acid volatile sulphide (AVS) concentrations.

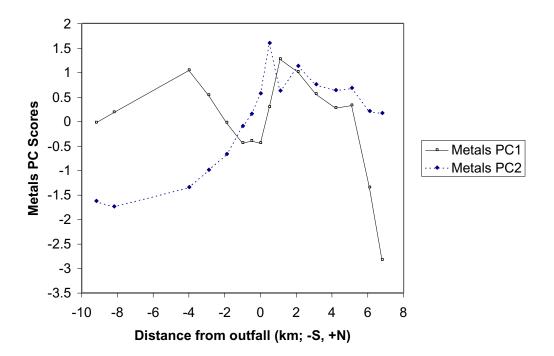
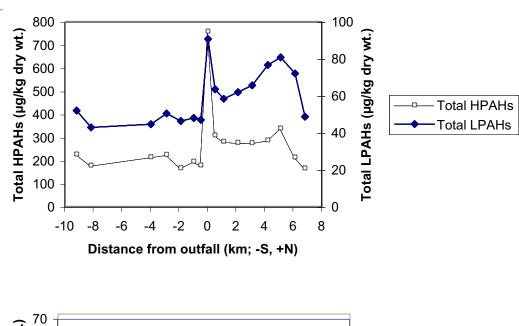


Figure 5. Spatial distributions of the first (Metals PC1) and second (Metals PC2) Principal Component scores derived from the analysis of metals concentrations in 2002.



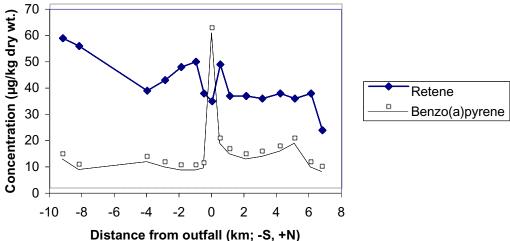


Figure 6. Spatial distribution of total LPAH and HPAH concentrations (top panel) and selected individual PAHs (bottom panel) in sediments.

The first two principal components for the organics (excluding PCBs) accounted for 63.4% of the total variation in the organic concentrations. Organics PC1 and Exposure PC1 were significantly positively correlated, but Organics PC2 was not associated to either Exposure PC1 or northings.

Compounds such as 4-nonylphenol and 1,4-dichlorobenzene were strongly correlated with Organics PC1. Other organics that were strongly correlated with Exposure PC1 were PAHs or estradiols/sterols that followed spatial distributions similar to Organics PC1. Note that retene, a PAH derived primarily from plant tissue, showed a different distribution (unrelated to effluent) than other PAHs (Figure 6, bottom panel).

Concentrations of PCBs, PCB congener groups, and Aroclors were positively correlated with the first principal component (PCB PC1) derived from 132 PCB compounds, which accounted for 75.5% of the total variation found among these parameters. PCB PC1 was significantly positively correlated with Exposure PC1. Spatial distributions for total PCBs and an individual PCB congener (coplanar PCB #77) are shown in Figure 7.

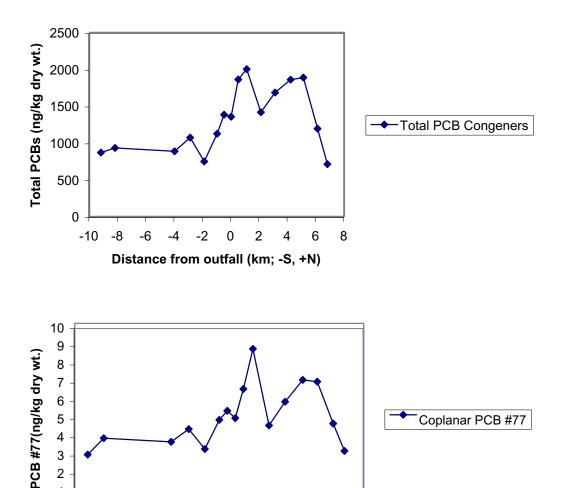


Figure 7. Spatial distribution of total PCBs (top panel) and coplanar PCB 77 (bottom panel).

-2

Distance from outfall (km; -S, +N)

0

2

4

6

8

Discussion

-10

-8

-6

Sediments collected in 2002 were composed primarily of fine-grained materials (silt and clay) except that higher proportions of sand were found at Stations 1 and 2 (6.1 to 6.8 km N of the outfall), Station 9 (outfall diffusers), and Station 16 (9.2 km S of the outfall). This pattern was similar to what was observed in 2001, and indicated that some stations may be influenced by sand deposition from the North Arm (Stations 1 and 2) and Main Arm (Station 15) of the Fraser River.

Sediment coliforms and coprostanol appeared to be excellent indicators of effluent exposure due to the high correlations with modelled annual maximum effluent-solids loads. In addition, their spatial concentrations varied at least 20-fold, and these variables are fairly specific to municipal sewage discharges (Bailey et al., 2003). 4-nonylphenol, epicoprostanol and cholestanol were also strongly correlated with exposure; spatial concentrations varied over 5-fold for these compounds. Finally, cadmium, mercury and silver exhibited strong positive correlations with the discharge, but comparatively low spatial variation (typically less than a factor of five). In general these results were consistent between 2000 and 2002.

Comparisons of sediment contaminant concentrations were made to marine sediment quality guidelines for the protection of aquatic life (CCME 1999; MWLAP 2001a, 2001b; USEPA 1991b) to evaluate the potential for adverse effects in the receiving environment.

Parameters that exceeded CCME or BCMWLAP values are presented in Table 4. There were no exceedences of the guidelines for cadmium, lead, mercury, zinc, silver, four chlorobenzene compounds, eight organochlorine pesticides, total PCBs, Aroclor 1254, 4-nonylphenol toxic equivalent units (TEQs), twelve individual PAHs, LPAH, HPAH and five phthalate esters.

No increases in frequency of exceedences were observed in 2002 relative to 2000 and 2001, with the exception of chrysene and fluoranthene, which each exceeded the CCME ISQG in one sample in 2002, compared with no exceedances in previous years. The number of exceedences for arsenic, chromium, and naphthalene were fewer than in previous years (Table 4); no exceedences were observed for ten other parameters that exceeded criteria in at least one sample in one or both of the prior years (8 individual PAHs, DDT and aldrin).

Table 4. Number of stations (out of 16) with exceedences of sediment quality guidelines in 2002. No exceedences were observed with a variety of other metals and organic parameters, as described in the text, including a number of parameters that exceeded guidelines in 2000 and/or 2001.

Parameter	Number of e	xceedences	Relative to 2000 and 2001	
	ISQG	PEL		
Arsenic	7	0	Fewer	
Chromium	7	0	Fewer	
Copper	16	0	Similar	
Nickel	16	1	Similar	
Chrysene	1	0	No previous exceedences	
Fluoranthene	1	0	No previous exceedences	
Naphthalene	5	0	Fewer	
Bis-(2-ethylhexyl) Phthalate	5	0	Similar	

Metals concentrations were also compared with those from a reference station in Loughborough Inlet, a British Columbia coastal fjord located about 200 km northwest of Vancouver, and with historical data for sediment constituents obtained in pre-discharge monitoring of the Iona Deep-Sea Outfall study area (Grindlay et al 1989). The reference site is remote from urban and industrial activity and provides an estimate of natural background conditions of surficial sediments. The measured concentrations of arsenic and nickel were similar to their SQGs, chromium concentrations were lower and copper was higher than their corresponding SQGs. The pre-discharge data indicated that the maximum arsenic, chromium and copper values were higher than the corresponding SQGs and exhibited similar ranges compared with post-discharge monitoring. Consequently, both reference site and pre-discharge data suggest that elevated concentrations of these metals may reflect background concentrations or inputs from other sources, such as the Fraser River. This is further supported by the results of the PCA, which demonstrated that Metals PC1 had a poor relationship with Exposure PC1. Conversely, concentrations of metals that appeared to be associated with the outfall (i.e., mercury, cadmium and silver) were below SQGs and within ranges observed in pre-discharge monitoring. These data suggest that there is an effluent "signature" for these metals, but that it is small relative to other inputs.

Historical and reference site data were generally not available with which to compare concentrations of organic chemicals, either because they were not measured or the detection limits were not sufficiently low. However, in general, there is no evidence of increasing concentrations of organic contaminants over time.

In summary, contaminant concentrations were generally low and exceedences of SQGs were few and relatively small. Metals that exceeded the SQGs were generally within the range of pre-discharge and reference site values. There was no evidence of increases in the concentrations of monitored parameters over time and, in fact, a number of parameters appear to have decreased between 2000 and 2002.

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References Cited

- APHA (American Public Health Association). 1998. *Standard Methods for the Examination of Water and Wastewater, 20th Edition*. American Public Health Association, American Water Works Association, and Water Environment Federation. Washington, DC.
- Bailey, H.C., C.A. McPherson, D. Hodgins, L. Fanning, M.D. Paine, B.J. Burd, V. Macdonald, G.G. Brooks, F. Chen,
 D. Brand and S. Raverty. 2003. *Iona Deep-Sea Outfall, 2001 Environmental Monitoring Program. Final Report.*Prepared for the Greater Vancouver Regional District (GVRD), Burnaby, BC by EVS Environment Consultants,
 North Vancouver, BC. January 2003. 344 pp. + appendices.
- CCME (Canadian Council of Ministers of the Environment). 1999. Chapter 6. Canadian sediment quality guidelines for the protection of aquatic life: Summary tables. **In**: *Canadian environmental quality guidelines*, 1999, Canadian Council of Ministers of the Environment, Winnipeg, MB.
- Chalaux, N., H. Takada, and J.M. Bayona. 1995. Molecular markers in Tokyo Bay sediments: sources and distribution. *Mar. Environ. Res.* **40**:77-92.
- Cretney, W. J., C.S. Wong, P.A. Christensen, B.W. McIntyre, and R.R. Fowler. 1980. Quantification of polycyclic aromatic hydrocarbons in marine environmental samples. In: *Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment*. B.K. Afaghan and D. McKay (eds). Environmental Science Research Series, Plenum Press, New York, NY.
- Cretney, W.J. Scientist, Contaminant Science Section, Department of Fisheries and Oceans, Institute of Ocean Sciences, Sidney, BC. Ongoing communications with Brian Fowler of Axys Analytical Services Ltd., Sidney, BC.
- Eganhouse, R.P., D.R. Olaguer, B.R. Gould, and C.S. Phinney. 1988. Use of molecular markers for the detection of municipal sewage sludge at sea. *Mar. Environ. Res.* **25**:1-22.
- Grindlay, P., E.A. Power and P.M. Chapman. 1989. *Iona deep sea outfall monitoring 1989, Study 1: evaluation of pre-discharge data.* Prepared for the Greater Vancouver Regional District by EVS Consultants Ltd., North Vancouver, BC. 71 pp + Appendices.
- GVRD. 2001. *Liquid Waste Management Plan, February 2001*. Greater Vancouver Regional District, Burnaby, BC. 55 pp.
- Hodgins, D.O., and S.L.M. Hodgins. 1999. *Iona Deep-Sea Outfall, 1999 Environmental Monitoring Program: Effluent Dispersion and Solids Deposition Modelling Study*. Prepared for the Greater Vancouver Regional District (GVRD), Burnaby, BC by Seaconsult Marine Research Ltd., Vancouver, BC. December 1999. 108 pp. + appendices.
- Hodgins, D.O., and S.L.M. Hodgins. 2000. Chapter 1: A re-evaluation of Iona effluent solids deposition based on sediment grain size characteristics. **In**: Development of a Receiving Environment Monitoring Approach to Liquid Waste Management, Progress Workshop 2, December 6, 2000, Support Materials Part 2 of 3: Iona WWTP Receiving Environment, Draft Technical Reports. Prepared for the Greater Vancouver Regional District, Burnaby, BC.
- Lee, H-B. and T.E. Peart. 1995. Determination of 4-nonylphenol in effluent and sludge from sewage treatment plants. *Anal. Chem.* **67**:1976-1980.
- McKeague, J.A. 1978. Manual on soil sampling and methods of analysis. 2nd ed. Canadian Society of Soil Science.
- McPherson, C.A., F. Landry, J. Wilcockson, B.J. Burd, S.E. Bertold, M.L. Fanning, M.C. Hamilton, G.G. Brooks, F. Chen and M. Gropen. 2001. *Iona deep-sea outfall, 2000 environmental monitoring program*. Prepared for the Greater Vancouver Regional District (GVRD), Burnaby, BC by EVS Environment Consultants Ltd., North Vancouver, BC and GVRD, Burnaby, BC. 156 pp.

- Mullin, M.D., D.M. Pochinl, S. McCrindle, M. Romkes, S.H. Safe, and L.M. Safe. 1984. High-resolution PCB analysis: synthesis and chromatographic properties of all 209 PCB congeners. *Environ. Sci. Technol.* **18**:468-476
- MWLAP (Ministry of Water, Land and Air Protection). 2001a. *British Columbia approved water quality guidelines* (criteria): 1998 edition, updated August 24, 2001. Prepared pursuant to Section 2(e) of the Environment Management Act, 1981. Ministry of Water, Land and Air Protection, Water Management Branch, Environment and Resource Management Department, Victoria, BC.
- MWLAP. 2001b. A compendium of working water quality guidelines for British Columbia: 1998 edition, updated August 23, 2001. Ministry of Water, Land and Air Protection, Water Management Branch, Environment and Resource Management Department, Victoria, BC.
- PSEP (Puget Sound Estuary Program). 1987. Recommended protocols for sampling and analyzing subtidal benthic macroinvertebrate assemblages in Puget Sound. Puget Sound Estuary Program. Prepared for U.S. Environmental Protection Agency, Seattle, WA. January, 1987. 31 pp.
- PSEP (Puget Sound Estuary Program). 1997. Recommended guidelines for sampling marine sediment, water column and tissue in Puget Sound. Puget Sound Estuary Program. Prepared for U.S. Environmental Protection Agency, Seattle, WA. April, 1997. 52 pp.
- Smith, L.M. 1981. Carbon dispersion glass fibres as an adsorbent for contaminant enrichment and fractionation. *Anal. Chem.* **53**:2154-2156.
- Stalling, D.L., Smith, L.M. and J.D. Petty. 1979. Approaches to comprehensive analyses of persistent halogenated environmental contaminants. pp. 302-323. **In**: *Measurement of Organic Pollutants in Water and Wastewater: ASTM STP 686*. C.E. Van Hall (ed.). American Society for Testing and Materials, Philadelphia, PA.
- USEPA (US Environmental Protection Agency). 1982. *Method 608. Organochlorine pesticides and PCBs. EPA-600/4-82-057, July 1982.* Environmental Monitoring and Support Laboratory, Cincinnati, OH.
- USEPA. 1986a. Test methods for evaluating solid waste, physical/chemical methods. Publication No. SW-846, 3rd ed., Washington, DC.
- USEPA. 1986b. *Method 8270C. Semivolatile organic compounds by gas chromatography/mass spectrometry (GC/MS), Revision 3, December 1996*. SW-846, 3rd ed., November 1986 (with Revision to Final Update III, December 1996). Office of Solid Waste and Emergency Response, Washington, DC.
- USEPA. 1991a. *Draft analytical method for determination of acid volatile sulphide in sediment*. U.S. Environmental Protection Agency, Office of Science and Technology, Washington, DC. August 1991.
- USEPA. 1991b. *Proposed sediment quality criteria for the protection of benthic organisms*: Endrin. US Environmental Protection Agency, Office of Water, Washington, BC.
- USEPA. 1999. *Method 1668, Revision A: Chlorinated biphenyl congeners in water, soil, sediment and tissue by HRCG/HRMS*. EPA-821-R-00-002, December 1999. Engineering and Analysis Division, Office of Water, Washington, DC.
- Walton, A. (ed.). 1978. *Methods for sampling and analysis of marine sediments and dredge materials. Ocean Dumping Report 1*, Department of Fisheries and the Environment, Ottawa, ON. pp. 17-25.
- Wilson, R.C.H., J.A.J. Thompson, M.B. Yunker, B.J. Burd, J.F. Garrett and D.G. Brand. 1999. *Iona Deep Sea Outfall, 1998 Environmental Monitoring Program, Post-Discharge Review.* Prepared for the Greater Vancouver Regional District by 2WE Associates Consultants Ltd., Salt Spring Island, BC. 97 pp.